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Solid-state polymer membranes for simple, sensitive, and low-cost monitoring of mercury in water

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Abstract

Solid-state Hg(II) selective membranes were produced and assessed by means of X-ray absorption near edge structure in the total reflection X-ray fluorescence (XANES -TXRF) setup and by the energy dispersive X-ray fluorescence (EDXRF) technique. Membranes were functionalized using four promising ligands for mercury complexation, i.e.: i) 4-(2-Pyridylazo) resorcinol (PAR), ii) thiourea, iii) calconcarboxylic acid (CCS), and iv) dithizone. A simple analytical procedure was followed, using miniscule reagent quantities, thus suggesting the process is also cost-effective. XANES -TXRF revealed that mercury complexes with the ligands, and not simply adsorbed onto the PVC matrix, while the complexation was not affected by the matrix existence. Mercury exhibited an increased oxidation grade and was covalently bound to

the ligand functional groups, via a strong chemical bond. EDXRF revealed that the solid-state membranes can be used for mercury speciation and trace analysis from environmental relevant matrices, such as tap water. The membranes could be a promising alternative to polymer inclusion membranes (PIMs), due to their simple configuration and high Hg (II) selectivity in aqueous media, but more research is needed. PAR appears to be the most promising ligand, followed by dithizone and thiourea. CCS had a minuscule preconcentration efficiency since it was preferably bound with Cu in tap water, indicating limited usefulness for mercury preconcentration. Therefore, it is suggested that, depending on the ligand, the solid-state membranes could also possibly used for multi-elemental heavy metals analysis in water.

Keywords: Divalent Mercury; mercury complexation; heavy metal pollution; The International Atomic Energy Agency (IAEA); Elettra Sinchrotron Trieste (EST); Synchrotron radiation-induced XANES

Introduction

The presence of mercury in natural water bodies is a growing environmental problem of emerging concern, since mercury is a toxic and hazardous heavy metal (Cooke-Andrews, 2006; European Environment Agency, 2018; Kallithrakas-Kontos and Foteinis, 2016). Mercury can be found hidden on numerous products, such as in mercury-containing skin creams and

soaps, dental amalgam, ethyl-mercury-containing vaccines, and latex paint additives. It is also released, on a large-scale, from power plants, e-waste/fluorescent lamps, wildfire emissions, and artisanal and small-scale gold mining (Budnik and Casteleyn, 2019). Exposure, even at trace levels ($\mu\text{g L}^{-1}$), is deemed a health hazard, since mercury bio-accumulates and can cause severe biological toxicity. As a result, the World Health Organization (WHO) has set the limit for water intended for human consumption at $1 \mu\text{g L}^{-1}$ Hg, while mercury has also been classified as one of the 33 “Priority pollutants” in the European Water Framework Directive (2000/60/EC) (Marguí et al., 2018).

Various analytical methods are available for the environmental monitoring of mercury, including voltammetry, mass spectrometry, atomic absorption or emission spectrometry, and chromatography, but most of them require a tedious sample pre-treatment, sophisticated performance, and/or expensive equipment (Ensafi and Fouladgar, 2006; Kallithrakas-Kontos and Foteinis, 2016). This implies the need for introducing fast, efficient, and low-cost methods for the determination of mercury in water matrices and at trace level concentration.

One such method for aqueous mercury preconcentration is the use of polymer-based membranes, functionalized with a promising ligand for aqueous mercury preconcentration. Currently, research is mainly focused on polymer inclusion membranes (PIMs), which are polymer-based liquid membranes that

were first introduced around 50 years ago as the sensing membrane in ion-selective electrodes and optodes and more recently have been used for aqueous mercury preconcentration (Almeida et al., 2017). However, these membranes could suffer from interferences from other ions, thus affecting their selectivity and sensitivity in aqueous Hg(II) preconcentration. To overcome such concerns we propose here the use of solid-state membranes for mercury preconcentration. Specifically, solid-state polymer-based membranes have been found versatile, selective, and easy to apply, since detection limits lower than $\mu\text{g}\cdot\text{L}^{-1}$ can be achieved with an energy dispersive X-ray fluorescence (EDXRF) (Hatzistavros and Kallithrakas-Kontos, 2014), a total reflection X-ray fluorescence (TXRF) technique (Aretaki et al., 2006; Koulouridakis and Kallithrakas-Kontos, 2004) or even with a benchtop TXRF system (Marguí et al., 2018).

Herein we comprehensively examine four promising ligands for Hg(II) complexation, i.e. 4-(2-Pyridylazo)resorcinol (PAR), thiourea, calconcarboxylic acid (CCS), and dithizone, which were successfully immobilized on the solid-state membrane matrix (i.e. PVC). Hg(II) is a soft Lewis acid, which preferentially bonds with soft Lewis bases, and therefore sulfur-containing chemicals, such as, thiourea, CCS, and dithizone, have been found effective in Hg adsorption from water matrices, since the thiol functional group is a soft base (Sun et al., 2018). Specifically, PAR, thiourea and dithizone are well-known ligands for mercury adsorption (Elly, 1973; Eshwar and Nagarkar,

1972; Litman et al., 1977; Zuo and Muhammed, 1995). Our group has also preliminary examined them for Hg(II) preconcentration, but only by means of TXRF (Aretaki et al., 2006; Koulouridakis and Kallithrakas-Kontos, 2004). Furthermore, CCS is a sulfur-containing chemical that we had successfully immobilized in selective membranes for aqueous ^{238}U and ^{234}U complexation (Kallithrakas-Kontos et al., 2018). Here we examine its sensitivity in aqueous Hg(II) preconcentration.

To study the chemical binding of aqueous Hg(II) ions in the solid-state functionalized membranes, TXRF-XANES was employed. Furthermore, EDXRF was used to quantitatively assess the membranes' Hg(II) preconcentration selectivity. Even though there are many works dealing with aqueous Hg(II) preconcentration approaches (Kallithrakas-Kontos and Foteinis, 2016; Pokhrel et al., 2017; Sun et al., 2018), a comprehensive chemical speciation study that could shed light on the nature of the chemical binding that it is formed between the aqueous Hg(II) ions and specific ligands immobilized on solid-state membranes is missing from the literature.

2. Materials and methods

2.1 Reagents and solvents

The membrane solution was prepared by mixing the following, high quality, analytical reagents. High molecular weight Polyvinyl chloride, popular known as PVC, was sourced from FlukaTM (no. 81387) and used as the

113 membrane matrix. PVC was mixed with: i) dibutyl phthalate (DBP), i.e. the
114 plasticizer, which was sourced from Riedel-de Haën (no. 36736, Pestanal®); ii)
115 Elman's reagent (5,5'-dithiobis-(2-nitrobenzoic acid), popular known as DTNB,
116 i.e. the ionophore, which was used to enhance anions binding properties on the
117 membrane surface and was sourced from Fluka™ (no. 43760); and finally iii)
118 the complexing agent (ligand), which was one of the following: a) 4-(2-
119 Pyridylazo)resorcinol (PAR), sourced from Fluka™ (no. 82970); b) thiourea,
120 sourced from Riedel-de-Haën™ (no. 33717); c) calconcarboxylic acid (CCS),
121 both anion and cation sourced from Merck (no 4595); and d) dithizone, sourced
122 from Sigma–Aldrich® (No. 43820). All chemical reagents were in solid form
123 and were diluted in tetrahydrofuran (THF), sourced from Sigma–Aldrich® (No.
124 401757). Ultrapure water (ASTM Type I) was used throughout the work, while
125 Fluka Mercury Standard for Atomic Absorption Spectroscopy AAS (Cat. No.
126 16482) was used for Hg(II) spiking.

127 **2.2 Membrane preparation procedure**

128 The functionalized membranes were prepared as a 10 uL solvent
129 containing 52% PVC, 32% DBP, 9.5% ligand and 6.5% DTNB, all diluted in
130 tetrahydrofuran (Hatzistavros and Kallithrakas-Kontos, 2014). For the EDXRF
131 analysis, each solvent was directly applied on thin-film substrates (Mylar® 2.5
132 µm). For solvent evaporation and membrane solidification, the film substrate
133 was left to dry in room temperature for 24 hours (alternatively an IR lamp can

be used for reduced drying time, but this was not required herein). Once prepared, the membranes were immersed on ultrapure water containing 50 $\mu\text{g L}^{-1}$ Hg(II) for 24 hours. During this time the Hg(II) - ultrapure water solution was kept stirred, as673 to enhance mercury ions mobility. After Hg(II) collection, the membranes were rinsed with high ultrapure and kept for analysis. All experiments were carried out at room temperature.

For the TXRF-XANES measurements, membrane solutions were prepared as described above. Then, 10 μL of each membrane solution was directly placed in the center of quartz reflectors, instead of the Mylar® 2.5 μm film, producing a 10-mm diameter spot. The reflectors containing the membranes were left to dry at room temperature and then immersed in the stirred Hg(II) - ultrapure water solution. The Hg(II) XANES spectrum was also obtained, to be used as a reference, by directly pipetting 10 μL of Hg(II) nitrate solution on a quartz reflector and left to dry at room temperature.

2.3 EDXRF analysis

For EDXRF measurements an AMETEK® SPECTRO XEPOS unit, which is widely used in environmental monitoring and assessment applications, was employed. A description of the unit can be found elsewhere (Foteinis et al., 2013; Hatzistavros and Kallithrakas-Kontos, 2014). In the context of this work the SPECTRO XEPOS Compton secondary/molybdenum mode (at 40 kV and 0.9 mA) was used under helium gas flushing, instead of in air atmosphere. Each

sample was irradiated for 5 min (300 s) and the measured raw data were processed with X-Lab Pro 4.0 quantitation software, using the TurboQuant screening method.

2.4 TXRF-XANES experiments

TXRF-XANES was employed to investigate whether i) mercury was simply adsorbed or was complexed with the ligand in the membrane and ii) the presence of the membrane matrix affected this complexation. Measurements were carried out at the X-ray Fluorescence beamline (10.1L) of Elettra Sincrotrone Trieste (EST), using the multi-technique X-ray spectrometry instrument developed by the International Atomic Energy Agency (IAEA Xspe) (Fig 1).

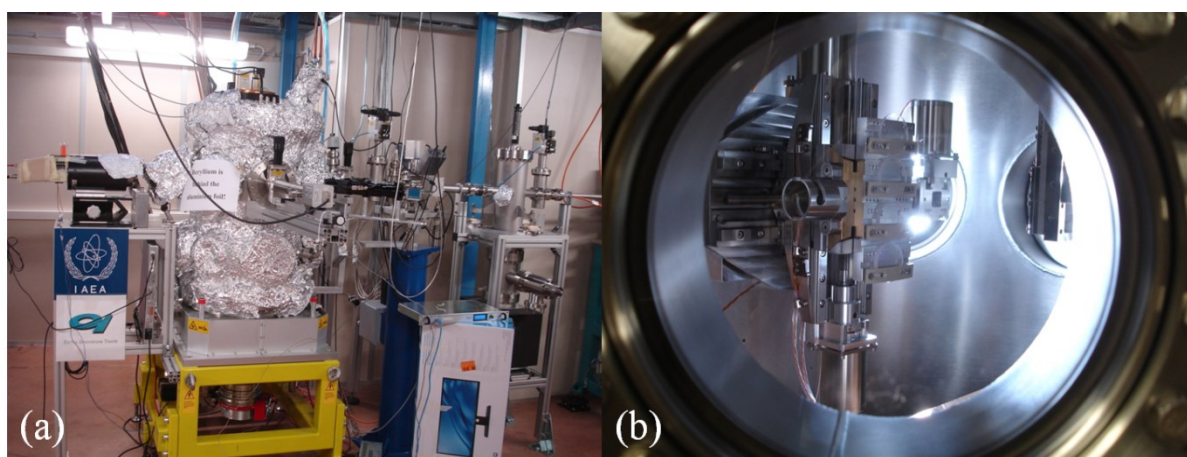


Fig 1: Picture of the: (a) IAEA Xspe instrument positioned at the 10.1L XRF beamline of Elettra Sincrotrone Trieste, and (b) Ultra High Vacuum chamber.

All the measurements were carried out in vacuum conditions, using a multi-axis motorized sample manipulator (Fig 1). More information concerning

the IAEA Xspe instrument hardware components and setup can be found elsewhere (Karydas et al., 2018; Marguí et al., 2018).

The XANES spectra were collected at the energy range of -50 to +200 eV around the Hg L₃ edge (12284 eV), in steps of 0.5 eV in the edge region and in steps of 2 and 1 eV in the pre- and post-edge regions, respectively. The spectra were collected in the TXRF detection mode. Raw data were processed using ATHENA software (Newville, 2001; Ravel and Newville, 2005). The pre-edge background of each spectra was subtracted, and the absorption coefficient was normalized to a unit-edge step. The low mercury concentration in the samples (the membranes were immersed in a solution containing 50 ug L⁻¹ mercury) and their limited thickness (thin films onto the TXRF sample supports), suggests that self-absorption correction for the XANES spectra could be omitted.

3. Results and Discussion

First XANES measurements are presented, as to identify the chemical environment of Hg(II) – ligand complexation. Thence, a comparative analysis between the solid-state membranes, in terms of Hg(II) preconcentration, is carried out by means of the EDXRF technique.

3.1 XANES results

TXRF-XANES was employed to investigate whether mercury is simply adsorbed in the membrane or complexes with the ligand and whether the presence of the membrane affects this complexation.

In order to answer the first question, the XANES spectra of the solid-state membranes were compared with the reference spectrum of Hg(II) nitrate. The normalized XANES spectra are shown in Fig. 2.

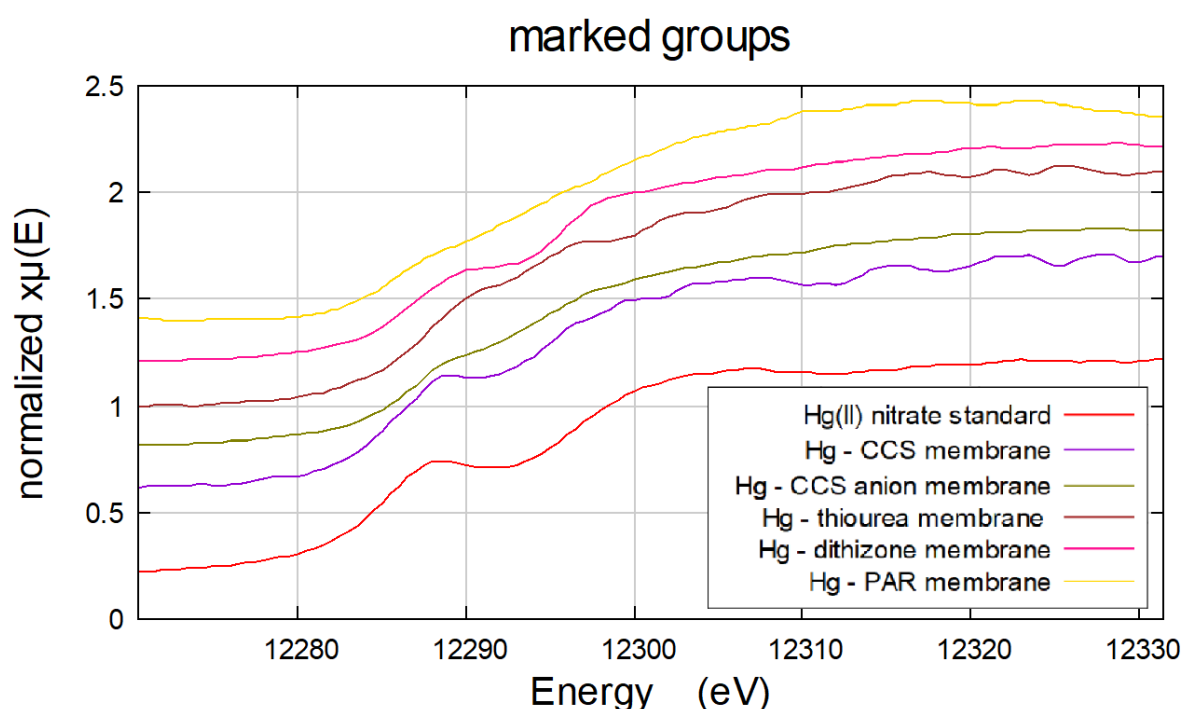


Fig. 2: Normalized Hg-L₃ TXRF-XANES spectra of the solid state membranes along with the reference spectrum of Hg(II) nitrate spectrum.

The spectra of Hg-CCS anion membrane presented a pronounced XANES feature (shoulder), which is also characteristic for the Hg(II) nitrate standard (Fig. 2). On the other hand, the absence of this feature at the spectra of Hg on the cation membranes (i.e. CCS cation, thiourea, dithizone and PAR), suggests

that Hg(II) is complexed with each ligand's functional groups into the PVC membrane, and not simply adsorbed.

To evaluate the possible PVC contribution forward the complexation procedure, the XANES spectrum of the Hg-dithizone was collected to be used as a reference and thence it was compared with the XANES spectrum of the dithizone functionalized membrane, which is PVC based (Fig. 3). The similarity between the Hg-dithizone reference spectrum and the one of the dithizone-functionalized PVC membrane permits the consideration that the presence of the membrane matrix (PVC) does not affect the complexation itself and seems to play a very small role during this procedure.

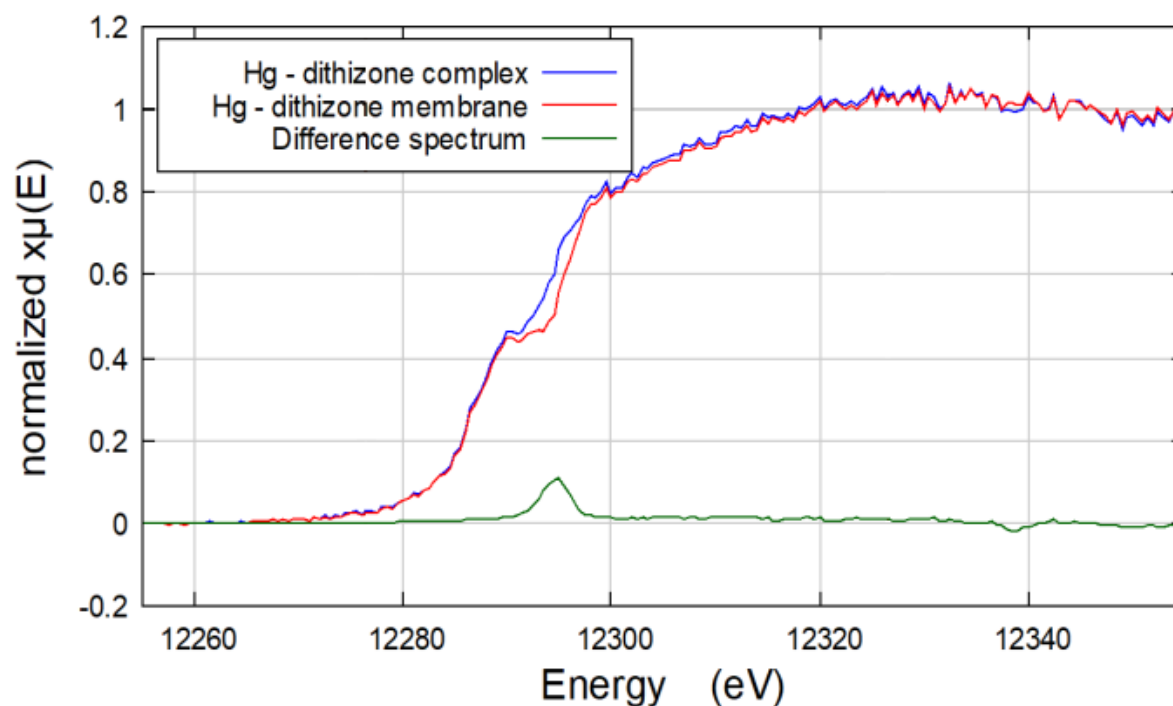


Fig. 3: Normalized TXRF-XANES spectra of Hg(II)-dithizone and the dithizone-functionalized PVC membrane and their difference

In order to get insight into the chemical state of mercury after its complexation with each ligand, the first derivative of each collected spectrum was calculated. The energy position of the first inflection point of normalized $\chi\mu(E)$ is considered as an indicator of the Hg oxidation state (Mishra et al., 2011; Rajan et al., 2008). Here, the position of the Hg L_3 edge in the membrane XANES spectra indicated by the maximum of the derivative (Fig. 4), is shifted towards higher energy, in an obvious manner, relative to that of the Hg(II) nitrate standard.

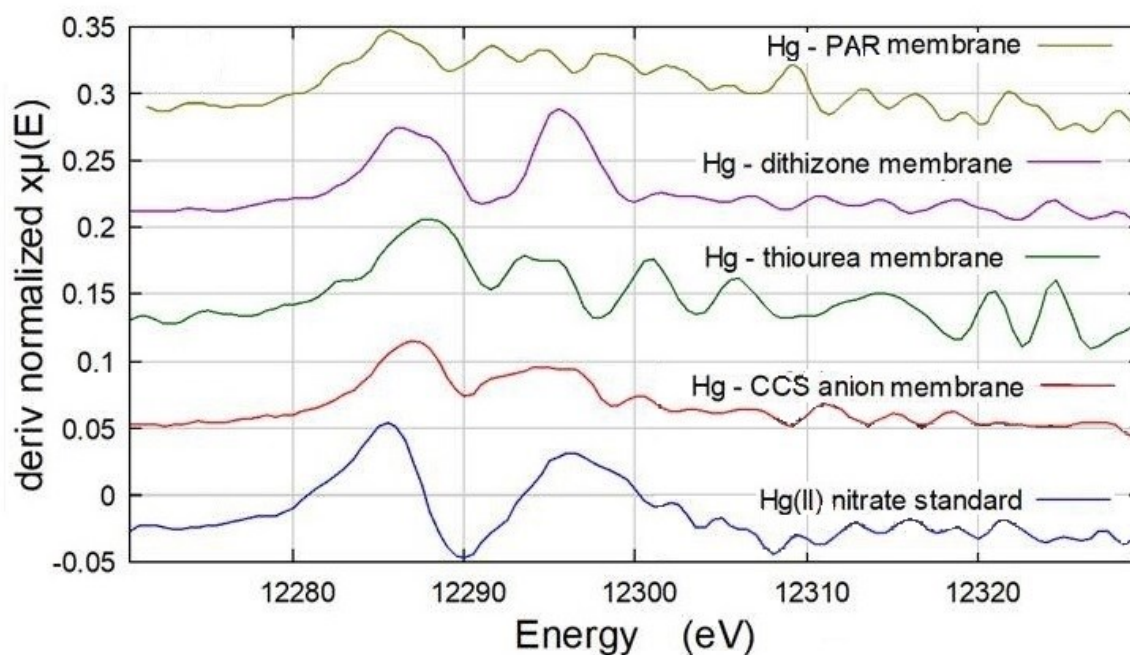


Fig. 4: First derivative of the Hg L_3 edge TXRF-XANES of anion and cation selective membranes, along with Hg(II) nitrate standard sample.

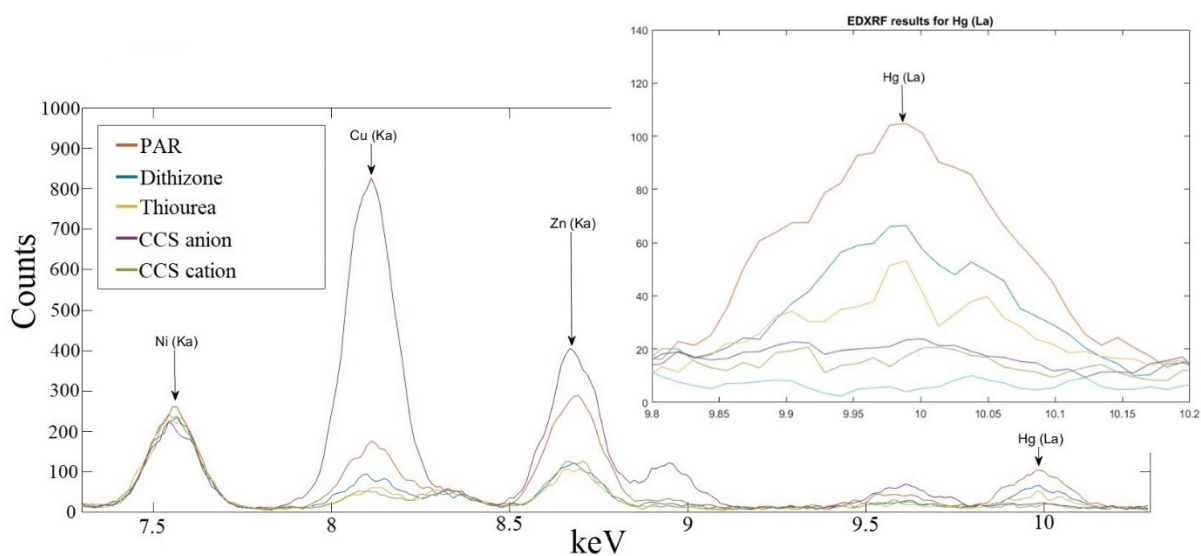
It can be observed that two main peaks exist in the Hg(II) nitrate and Hg dithizone membrane spectra, while in the remaining spectra the second main peak is subtle (Fig. 4). The energy difference between them (ΔE) has been

correlated with the bonding environment of the probed element (Colombo et al., 2014; Powers, 1982). From Fig. 4 it can be observed that the ΔE for Hg(II) nitrate standard 11.0 eV, while the ΔE for the dithizone, PAR, CCS anion, thiourea 9.0, 7.2, 8.4 eV, respectively. In general, large ΔE values correspond to Hg-ligand complexes with ionic character, while a small ΔE values are correlated with complexes having a more covalent character (Colombo et al., 2014; Powers, 1982). Therefore, results imply that Hg(II) was covalently bound to all ligands functional groups via a strong chemical bond. Finally, the differences between the Hg(II) nitrate standard and the solid-state membranes mainly lie to the different position of the main peak and the ΔE between the two main peaks, which reveal the slightly different oxidation state of the Hg.

3.2 EDXRF results

In our previous works, solid-state PVC-based functionalized membranes were studied in terms of mercury preconcentration efficiency and were found promising (Aretaki et al., 2006; Hatzistavros and Kallithrakas-Kontos, 2014; Koulouridakis and Kallithrakas-Kontos, 2004; Marguí et al., 2018). Here, four different functionalized membranes, i.e. dithizone, PAR, thiourea, and CCS (both anion and cation) were examined by EDXRF. In order to comprehensively examine and acquire an in-depth understanding of each functionalized membrane efficiency in environmental relevant water matrices, mercury preconcentration took place in tap water instead of ultrapure water.

The reason that tap water was chosen over ultrapure water is twofold. Firstly, mercury monitoring and assessment in tap water comprise a common environmental problem. Secondly, apart from the spiked mercury content, tap water contains a wide array of other (heavy) metals and elements, which could have different affinities with each ligand, thus possibly affecting the selective preconcentration of mercury. Specifically, as mentioned above the ligands under study are sensitive to a vast spectrum of heavy metals, apart from mercury, as well as other metals and elements typically found in environmental relevant samples. Therefore, when the membranes are exposed to environmental relevant matrices each ligand could have a strong affinity towards other (heavy) metals, thus reducing the selectivity in preconcentrating mercury. Fig. 5 shows the comparison of EDXRF spectra for functionalized membranes, highlighting mercury preconcentration efficiency, as well as their affinity towards Ni, Cu, and Zn, which were present in the tap water used.



266 Figure 5: Section of EDXRF spectra for the non-functionalized membrane (light blue colour)
267 compare to the membrane functionalized with a) PAR (red colour)), thiourea (yellow colour),
268 CCS anion (purple colour), CCS cation (green colour), and dithizone (blue colour). Inset:
269 Zoom on the EDXRF results for mercury, i.e. Hg(La).

270 As observed in Fig. 5, membrane functionalization has a profound effect in
271 aqueous Hg(II) sorption. It was found that the PAR functionalized membrane
272 yielded, by and large, the higher sensitivity in aqueous Hg(II) preconcentration,
273 followed by dithizone and thiourea. Specifically, we have established that for the
274 dithizone-functionalized membrane the aqueous mercury detection limit is and
275 0.069 ng mL^{-1} for doped ASTM Type I water and seawater, respectively (1000
276 mL sample volume, with 24 h equilibration time and 300 s irradiation time).
277 The obtained results (Fig. 5) suggest that PAR could achieve a 66 % lower, i.e.
278 better, detection limit, while thiourea appears to have about 25% higher, i.e.
279 worse, detection limit. However, the exact performance and detection limits of
280 each membrane will be further examined in our future works. Finally, results
281 are suggestive that both the anion and cation CCS membranes had very low
282 efficiency in preconcentrating aqueous Hg(II). Nonetheless, it was identified that
283 the CCS cation membrane has a very high affinity towards Cu, and to a smaller
284 degree towards Zn, both abundant in the tap water used in the present study.
285 This possibly grossly affects the selectivity of the CCS cation membrane in
286 Hg(II) selective preconcentration. The above suggests that CCS usefulness for
287 mercury monitoring and assessment in natural water bodies is limited. However,

it could be an excellent indicator for other (heavy) metals found in environmental relevant matrices.

Therefore, results indicate that the most promising, by and large, ligand for aqueous Hg(II) preconcentration is PAR. Dithizone performed better than thiourea, which exhibited around $\sim 29\%$ lower Hg (II) preconcentration efficiency compared to dithizone. Results for CCS (both anion and cation) were not encouraging for its use for aqueous Hg(II) preconcentration, however, it appears that it could act as a promising indicator for other (heavy) metals typically found in natural water matrices.

3.3 Interferences with other ions and environmentally relevant applications of the functionalized membranes

The solid-state membranes were proved to be a relatively simple medium for aqueous Hg(II) monitoring and assessment. Furthermore, once the membranes are prepared, they can be used both in the laboratory but also on the field by non-specialized personnel, due to their small size and simple configuration with no moving parts (Fig. 6). This assumption was tested by using the solid-state membranes at the easiest possible level. Specifically, in this scenario analytical accuracy was set in second place in order to examine the selectivity and Hg(II) detection limit when the membranes are used by non-specialized personnel. As such, each membrane was simply submerged for 24 h in 1 L of bottled water, containing $100\text{ }\mu\text{g L}^{-1}$ Hg(II). The water was

not stirred, which enhances mercury ions mobility and thus lowering Hg (II) detection limit, to account for cases where the membranes are used directly on the field with limited means.

Furthermore, bottled water was examined, which is an environmentally relevant water matrix rich in ions that could hamper membrane selectivity in Hg(II). Specifically the bottle water main characteristics were pH 8.0, 290 $\mu\text{S cm}^{-1}$, 134 mg L^{-1} (CaCO_3), 31 mg L^{-1} Ca^{+2} , 14 mg L^{-1} Mg^{+2} , 7 mg L^{-1} Na^+ , 160 mg L^{-1} HCO_3^- , 13 mg L^{-1} Cl^- .

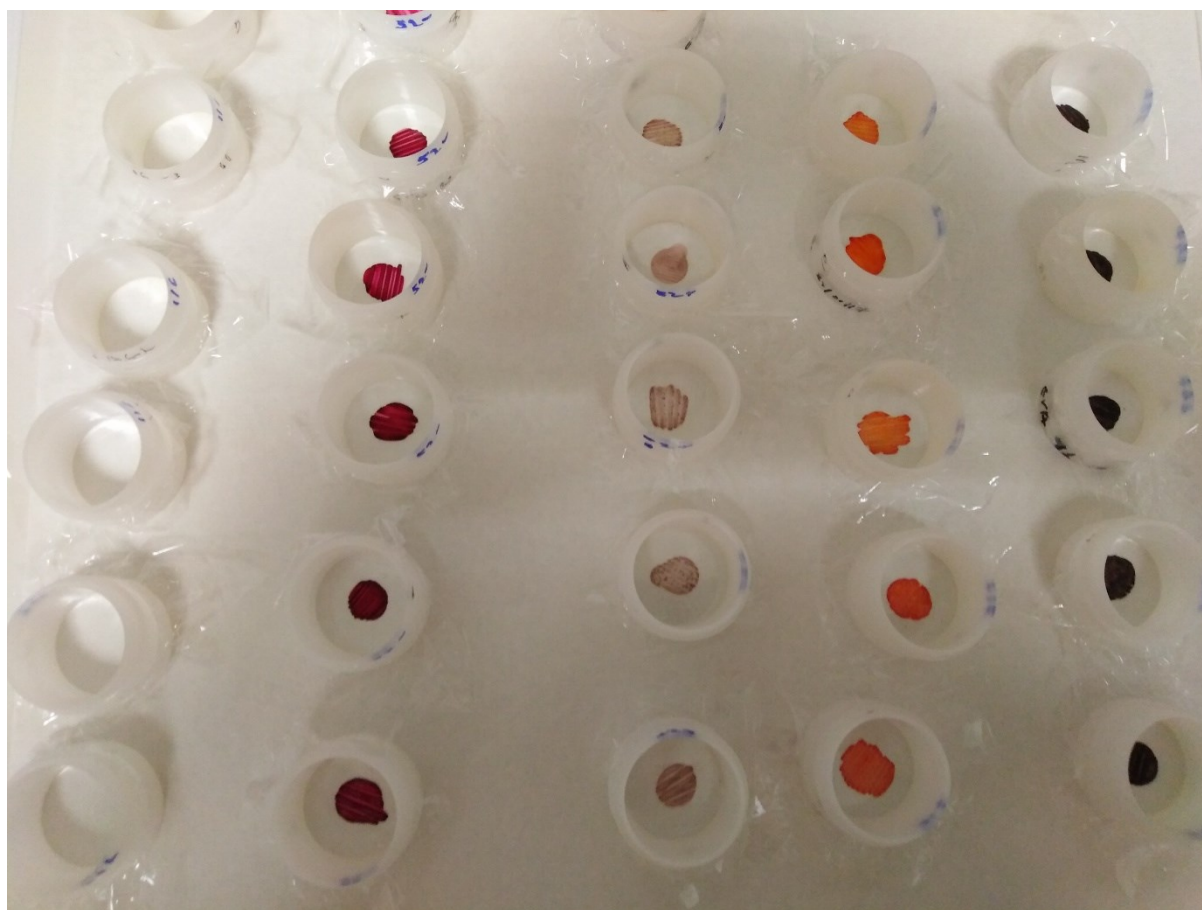


Figure 6: The prepared solid-state membranes.

Table 1 list the identified detection limits (DL) when using the simplest membrane configuration. DL was estimated by dividing the net intensity with the sensitivity in counts per second per percent (Van Grieken and Markowicz, 2001). It can be observed that even though bottled water contained a large number of ions, which could interfere with Hg(II) selectivity, the solid-state membranes yielded very low detection limits using the simplest configuration, i.e. just submerging the membranes in the water without stirring.

It was found that in the case of bottled water PAR gave the lowest DL, by and large, followed by dithizone, thiourea, CCS anion, and finally CCS cation. Results are in agreement with those obtained in tap water, which was expected since both water matrices are quite similar. However, the most important fact is that even when using the solid-state membranes at the possible simplest configuration, very low DL are achieved, which are on par or even lower than the 1 ug L^{-1} limit set by the World Health organization (WHO) for water intended for human consumption (Marguí et al., 2018). Therefore, it is possible to use the solid-state membranes on the field and thence just mail them to the laboratory for the EDXRF measurements, especially when taking into account their small size (Fig. 6). Overall, results suggest that the produced solid-state membranes could be promising for real-world applications and possibly an alternative to liquid membranes, such as the polymer inclusion

membranes (PIMs) which are largely employed for mercury monitoring and assessment applications. However, more research is need towards that end.

Table 1: The achieved detection limits for bottled water. Irradiation time 4,200 sec.

Membrane	Detection limit ($\mu\text{g L}^{-1}$)
Dithizone	1.9
CCS-	5
CCS+	13.3
PAR	0.88
Thiourea	3.25

Furthermore, the method can be characterized as cost-effective since, compared to other analytical techniques, EDXRF is a relatively low-cost technique, which is also the chemical reagents used for membrane preparation. Specifically, PAR, the most promising ligand, is a well-known and low-cost chemical reagent (Liu et al., 2012). This is also the case for all chemical reagents utilized herein towards producing the functionalized membranes, which are in general characterized by low-cost and are easy to find and purchase.

Finally, PAR, apart from being the most promising indicator for aqueous Hg(II), is also an excellent indicator for many other heavy metal ions, such as Co^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} and Cu^{2+} (Liu et al., 2012). This is the case for thiourea, CCS, and dithizone, which are also sensitive to a vast spectrum of heavy metals. Therefore, it is suggested that the novel functionalized

membranes can be used for multi-elemental or selective analyses of (heavy) metals in water matrices, which will be examined in our future works. Given the fast, simple, and low-cost membrane preparation method, it is suggested that the functionalized membranes can act as a fast, efficient, and low-cost indicator for mercury, and possibly other heavy metals, monitoring and assessment in natural water bodies. Future applications could also include the mercury and heavy metal collection, not only from natural waterbodies but also from industrial heavy metal hotspots, provided that the membranes are produced and used in large-scale routine works.

4. Conclusions

Here we introduced, studied, and assessed a simple, sensitive, and low-cost method for Hg(II) monitoring and assessment in water matrices, and even at trace level. Solid-state membranes were successfully functionalized either with i) thiourea, ii) PAR, iii) CCS or iv) dithizone, using as a membrane matrix PVC.

TXRF-XANES results revealed that mercury complexes with each of the selected ligands, rather than simply adsorbed in the membrane matrix. Using the EDXRF technique each membrane was quantitatively assessed in terms of Hg(II) preconcentration efficiency. It was found that membrane functionalization has a profound effect in Hg(II) preconcentration, with PAR appearing to have, by and large, the highest efficiency in mercury

378 preconcentration. Thiourea exhibited around 29 % lower preconcentration
379 compared to dithizone, but both had a significantly lower Hg(II)
380 preconcentration efficiency compared to PAR. CCS (both anion, but
381 particularly cation) gave poor efficiencies, suggesting that its use for aqueous
382 Hg(II) preconcentration is limited.

383 When using the membranes at their simple configuration, i.e. just immerse
384 them in a water matrix, very low detection limits are achieved. Furthermore, the
385 solid-state membranes were found to perform very well in environmentally relevant
386 matrices, such as tap and bottled water, even though they contain a large
387 number of anions. Results suggest that the solid-state membranes can act as a
388 simple, sensitive, and low-cost indicator not only for aqueous mercury, but
389 possibly for other (heavy) metals, implying that they could be used for multi-
390 elemental analysis in environmentally relevant water matrices.

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PAR is a well-known (Eshwar and Nagarkar, 1972)

6. References

- Almeida MIGS, Cattrall RW, Kolev SD. Polymer inclusion membranes (PIMs) in chemical analysis - A review. *Analytica Chimica Acta* 2017; 987: 1-14.
- Aretaki IN, Koulouridakis P, Kallithrakas-Kontos N. Total reflection X-ray fluorescence mercury analysis after immobilization on quartz surfaces. *Analytica Chimica Acta* 2006; 562: 252-257.
- Budnik LT, Casteleyn L. Mercury pollution in modern times and its socio-medical consequences. *Science of The Total Environment* 2019; 654: 720-734.
- Colombo MJ, Ha J, Reinfelder JR, Barkay T, Yee N. Oxidation of Hg(0) to Hg(II) by diverse anaerobic bacteria. *Chemical Geology* 2014; 363: 334-340.
- Cooke-Andrews J. Mercury Speciation in the Environment Using X-ray Absorption Spectroscopy. In: Atwood DA, editor. *Recent Developments in Mercury Science*. Springer Berlin Heidelberg, Berlin, Heidelberg, 2006, pp. 1-35.
- Elly CT. Dithizone Procedure for Mercury Analysis. *Journal (Water Pollution Control Federation)* 1973; 45: 940-945.
- Ensafi AA, Fouladgar M. Development of a mercury optical sensor based on immobilization of 4-(2-pyridylazo)-resorcinol on a triacetylcellulose membrane. *Sensors and Actuators B: Chemical* 2006; 113: 88-93.
- Eshwar MC, Nagarkar SG. Photometric determination of mercury(II) with 4-(2-Pyridylazo)-resorcinol. *Fresenius' Zeitschrift für analytische Chemie* 1972; 260: 289-289.
- European Environment Agency E. Mercury in Europe's environment - A priority for European and global action. *EEA Report No 11/2018*, 2018.
- Foteinis S, Kallithrakas-Kontos NG, Synolakis C. Heavy Metal Distribution in Opportunistic Beach Nourishment: A Case Study in Greece. *The Scientific World Journal* 2013; 2013: 5.
- Hatzistavros VS, Kallithrakas-Kontos NG. X-ray fluorescence mercury determination using cation selective membranes at sub-ppb levels. *Analytica Chimica Acta* 2014; 809: 25-29.
- Kallithrakas-Kontos N, Foteinis S. Recent Advances in the Analysis of Mercury in Water - Review. *Current Analytical Chemistry* 2016; 12.
- Kallithrakas-Kontos NG, Xarchoulakos DC, Bouladaki P, Potiriadis C, Kehagia K. Selective Membrane Complexation and Uranium Isotopes Analysis in Tap Water and Seawater Samples. *Analytical Chemistry* 2018; 90: 4611-4615.
- Karydas AG, Czyzycki M, Leani JJ, Migliori A, Osan J, Bogovac M, et al. An IAEA multi-technique X-ray spectrometry endstation at Elettra Sincrotrone Trieste: benchmarking results and interdisciplinary applications. *Journal of Synchrotron Radiation* 2018; 25: 189-203.

Koulouridakis PE, Kallithrakas-Kontos NG. Selective Mercury Determination after Membrane Complexation and Total Reflection X-ray Fluorescence Analysis. *Analytical Chemistry* 2004; 76: 4315-4319.

Litman R, Williams ET, Finston HL. Extraction of mercury by dithizone and stability of the extracted complex. *Analytical Chemistry* 1977; 49: 983-987.

Liu T, Li G, Zhang N, Chen Y. An inorganic–organic hybrid optical sensor for heavy metal ion detection based on immobilizing 4-(2-pyridylazo)-resorcinol on functionalized HMS. *Journal of Hazardous Materials* 2012; 201-202: 155-161.

Marguí E, Queralt I, Guerra M, Kallithrakas-Kontos N. Mercury determination at trace levels using membrane preconcentration and benchtop total reflection X-ray fluorescence analysis. *Spectrochimica Acta Part B: Atomic Spectroscopy* 2018; 149: 84-90.

Mishra B, O’Loughlin EJ, Boyanov MI, Kemner KM. Binding of HgII to High-Affinity Sites on Bacteria Inhibits Reduction to Hg0 by Mixed FeII/III Phases. *Environmental Science & Technology* 2011; 45: 9597-9603.

Newville M. IFEFFIT : interactive XAFS analysis and FEFF fitting. *Journal of Synchrotron Radiation* 2001; 8: 322-324.

Pokhrel LR, Ettore N, Jacobs ZL, Zarr A, Weir MH, Scheuerman PR, et al. Novel carbon nanotube (CNT)-based ultrasensitive sensors for trace mercury(II) detection in water: A review. *Science of The Total Environment* 2017; 574: 1379-1388.

Powers L. X-ray absorption spectroscopy Application to biological molecules. *Biochimica et Biophysica Acta (BBA) - Reviews on Bioenergetics* 1982; 683: 1-38.

Rajan M, Darrow J, Hua M, Barnett B, Mendoza M, Greenfield BK, et al. Hg L3 XANES Study of Mercury Methylation in Shredded Eichhornia crassipes. *Environmental Science & Technology* 2008; 42: 5568-5573.

Ravel B, Newville M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 2005; 12: 537-541.

Sun M, Cheng G, Ge X, Chen M, Wang C, Lou L, et al. Aqueous Hg(II) immobilization by chitosan stabilized magnetic iron sulfide nanoparticles. *Science of The Total Environment* 2018; 621: 1074-1083.

Van Grieken R, Markowicz A. *Handbook of X-Ray Spectrometry*: CRC Press, 2001.

Zuo G, Muhammed M. EXTRACTION OF MERCURY(II) BY THIOUREA-BASED REAGENTS. *Solvent Extraction and Ion Exchange* 1995; 13: 855-878.